3 KEY ANALYTICAL PLANNING ISSUES AND DEVELOPING ANALYTICAL PROTOCOL SPECIFICATIONS

3.1 Introduction

This chapter provides an overview of key analytical planning issues that should be addressed and resolved during a directed planning process (see Chapter 2). The resolution of these issues results in the development of Analytical Protocol Specifications (APSs). *A key analytical planning issue may be defined as one that has a significant effect on the selection and development of analytical protocols, or one that has the potential to be a significant contributor of uncertainty to the analytical process and, ultimately, the resulting data*. It should be noted that a key analytical planning issue for one project may not be a key issue for another project. From an analytical perspective, one of the most important functions of a directed planning process is the identification and resolution of these key issues for a project.

In accordance with a performance-based approach, APSs only should contain the minimum level of specificity required to meet the project or program data requirements and resolve the key analytical planning issues. Identification and resolution of these issues should be an integral part of a directed planning process, and the APSs should be an output or product of that process. This chapter provides a focused examination of analytical planning issues and the development of APSs.

In order to assist the project planning team in identifying key issues, this chapter provides a list of potential key analytical planning issues. Neither the list nor discussion of these potential issues is an exhaustive examination of all possible issues for a project. However, this chapter does provide a framework and a broad base of information that can assist in the identification of key analytical planning issues for a particular project during a directed planning process.

Analytical planning issues can be divided into two broad categories—those that tend to be matrix-specific and those that are more general in nature. While there is certainly some overlap between these two broad categories, MARLAP divides analytical planning issues along these lines because of the structure and logic it provides in developing APSs. This approach involves identifying key analytical planning issues from the general (non-matrix-specific) issues first and then proceeding on to the matrix-specific issues. Examples of non-matrix-specific analytical planning issues include sample tracking and custody issues. These general issues are discussed in detail in Section 3.3. Examples of matrix-specific issues include filtration and preservation issues of water samples. Matrix-specific analytical planning issues will be discussed in detail in Section

3.4. Section 3.5 provides guidance on assembling the APSs from the resolution of these issues. Section 3.6 discusses defining the level of protocol performance demonstration required for a particular project, and Section 3.7 discusses incorporating the APSs into the project plan documents.

3.2 Overview of the Analytical Process

Identifying key analytical issues for a particular project requires a clear understanding of the analytical process. The analytical process as described in Chapter 1 includes all activities, starting with field sample preparation and preservation, followed by sample receipt and inspection, laboratory sample preparation; sample dissolution; chemical separations; instrument measurements, data reduction and reporting, and sample tracking and quality control of the process. Figure 3.1 illustrates the analytical process. It should be noted that a particular project's analytical process may not include all of the activities listed above. For example, if the project's analytical process involves performing gamma spectrometry on soil samples, sample dissolution and chemical separation activities normally are not required. Each step of a particular analytical process contains potential planning issues that may be key analytical planning issues depending on the nature and data requirements of the project. Therefore, it is important to identify the relevant activities of the analytical process for a particular project early in the directed planning process. Once the analytical process for a particular project has been established, key analytical planning issues, including both general and matrix-specific ones, can be identified.

3.3 General Analytical Planning Issues

This section discusses a number of general analytical planning issues that are common to many types of projects and are often key planning issues, depending on the nature and data requirements of the project. (Section 6.5 of Chapter 6 also discusses a number of these planning issues to provide context on the method selection process.) This section presents each planning issue as an activity to be accomplished during a directed planning process and also identifies the expected outcome of the activity in general terms. The resolution of these general analytical planning issues, particularly those that are key planning issues for a project, provides the basic framework of the APSs and, therefore, should be identified and resolved before proceeding to matrix-specific planning issues. Normally the resolution of these issues results, at a minimum, in an analyte list, identified matrices of concern, measurement quality objectives (MQOs), and established frequencies and acceptance criteria for quality control (QC) samples. The resolution of matrix-specific issues, particularly those that are key issues for a project, normally provides the necessary additions and modifications to the basic framework of the APSs needed to complete and finalize the specifications. MARLAP recommends that any assumptions made

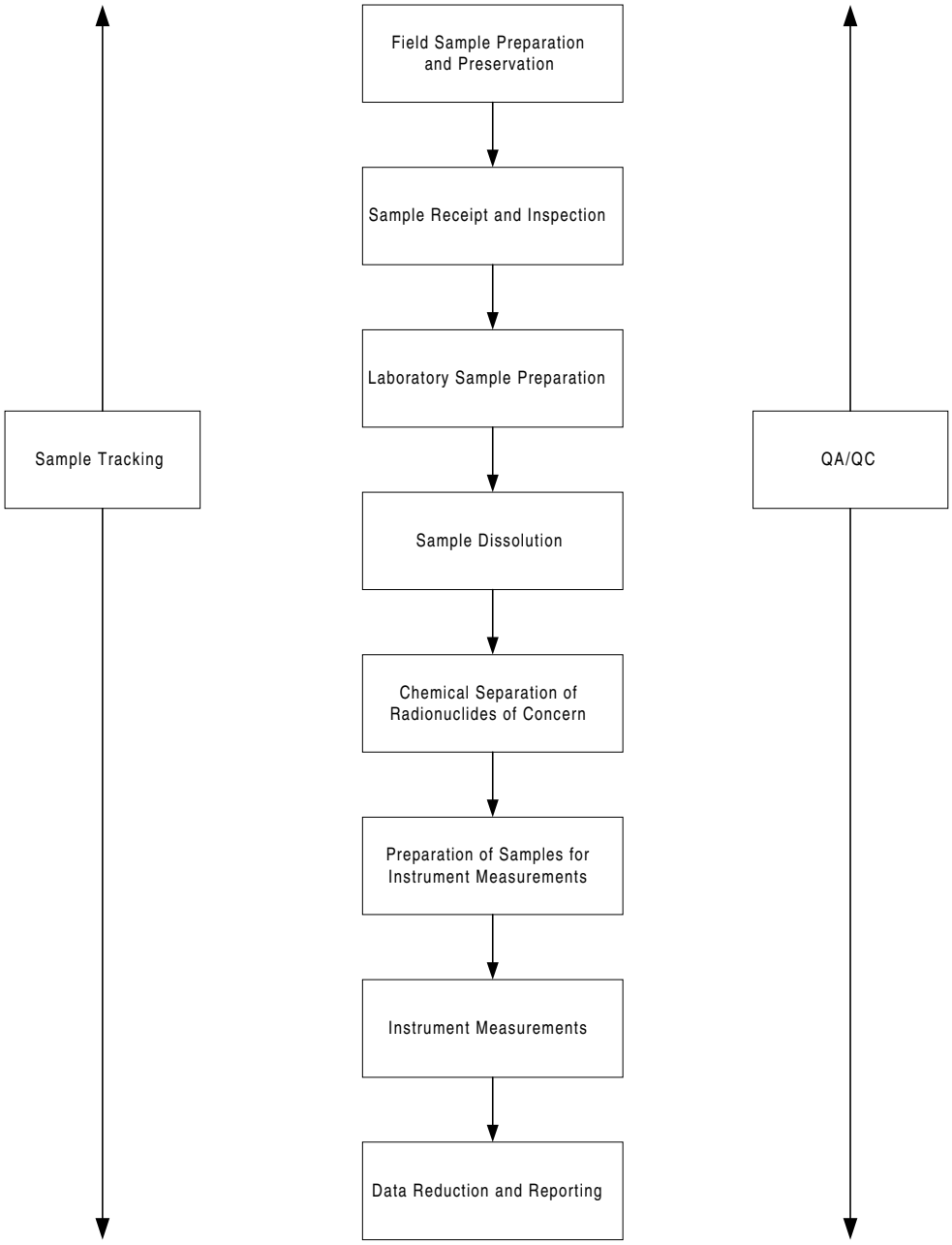

Figure 3.1 — Typical components of an analytical process

during the resolution of key analytical planning issues are documented, and that these assumptions are incorporated into the appropriate narrative sections of project plan documents. Documenting these assumptions may help answer questions or help make decisions during the implementation and assessment phases of the project.

3.3.1 Develop Analyte List

From an analytical perspective, one of the most important planning issues that should be addressed very early in a directed planning process by the project planning team is the target analyte list—the radionuclides of concern for the project. For many projects, data are available from previous activities for this purpose. Four possible sources of information are (1) historical data, (2) process knowledge, (3) previous studies, and (4) information obtained from conducting a preliminary survey or characterization study. Although discussed separately in Section 3.3.3, the identification and characterization of matrices of concern is often done concurrently with the development of an analyte list.

Historical data are one source of existing information. Many activities associated with radioactive materials have been well-documented. For example, activities licensed by the Nuclear Regulatory Commission (NRC) or NRC Agreement States normally generate much documentation. Chapter 3 of MARSSIM (2000) provides guidance on obtaining and evaluating historical site data.

Another source of existing information is process knowledge. Some sites are associated with a specific activity or process that involved radioactive material, where the process was well-defined and the fate of the radioactive material in the process was known or controlled. Examples include uranium and rare earth ore processing, operations at Department of Energy (DOE) weapons facilities, and operations at commercial nuclear power plants. (See Section 6.5.2 of Chapter 6 for additional discussion on process knowledge.)

A third source of existing information is previous studies. Similar projects or studies of related topics can provide valuable information during a directed planning process. Previous studies may provide useful information on background radiation. Many radionuclides are present in measurable quantities in the environment. Natural background radiation is due both to primordial and cosmogenic radionuclides. Anthropogenic background includes radionuclides that are ubiquitous in the environment as a result of such human activities as the atmospheric testing of nuclear weapons. Natural and anthropogenic backgrounds can be highly variable even within a given site. It may be important to consider the background and its variability when choosing an action level

and when establishing the MQOs. Every effort should be made to obtain as much existing information as possible *prior* to initiating a directed planning process.

Sometimes there are little or no historical data that can help identify radionuclides or the concentration range of potential concern, or the existing data may be of inadequate quality. In these cases, it may be necessary to perform preliminary analyses to identify the radionuclides of concern or their concentration range. A fourth source of information is generated by conducting a preliminary survey or characterization study. The design of preliminary surveys or characterization studies should be part of the project planning process. The need for fast turnaround and lower costs at this stage of the project may lead to different data quality objectives (DQOs) and MQOs that are less restrictive than those used for the primary phase of the project. However, it is important that analytical requirements for the survey or study be established during the project planning process. Gross alpha, gross beta, and gamma spectrometry analyses often are used for preliminary survey or characterization studies.

The benefits of performing these types of measurements include:

- Rapid analysis and short turnaround time;
- Relatively low analytical costs; and
- Detecting the presence of a wide range of radionuclides in a variety of media.

There are also limitations on the use of these analyses. These limitations include:

- No specific identification for pure alpha- or pure beta-emitting radionuclides and low-energy, gamma-emitting radionuclides are generally not identified; and

- Failing to identify the presence of several radionuclides (e.g., ^{3}H and other volatile radionuclides; ^{55}Fe and other radionuclides that decay by electron capture).

OUTPUT: An initial list of radionuclides of potential concern including a brief narrative explaining why each radionuclide is on the list as well as an explanation of why certain radionuclides were considered but not listed. This list may be modified as more project-specific information becomes available. It is better to include radionuclides on the initial list even if the probability that they significantly contribute to the addressed concerns is small. The consequence of discovering an additional radionuclide of concern late in a project generally outweighs the effort of evaluating its potential during planning.

3.3.2 Identify Concentration Ranges

Once the radionuclides of concern have been identified, the expected concentration range for each radionuclide should be determined. Historical data, process knowledge, and previous studies, if available, can be used to determine the expected concentration range for each analyte. While most analytical protocols are applicable over a fairly large concentration range for the radionuclide of concern, performance over a required concentration range can serve as an MQO for the protocol selection process and some analytical protocols may be eliminated if they cannot accommodate the expected concentration range. In addition, the expected concentration ranges of all of the radionuclides of concern can provide useful information about possible chemical and spectral interferences. For example, while an analytical protocol for a particular radionuclide may be able to accommodate the expected concentration range for that radionuclide, the concentrations of other radionuclides may present interference problems, thus eliminating the use of that analytical protocol.

OUTPUT: The expected concentration range for each radionuclide of concern as well as the expected concentration range of any potential chemical or radiological interference.

3.3.3 Identify and Characterize Matrices of Concern

During a directed project planning process, the matrices of concern should be clearly identified. For many projects, typical matrices may include surface soil, subsurface soil, sediment, surface water, groundwater, drinking water, air particulates, biota, structural materials, metals, etc. Historical data, process knowledge, previous studies, conceptual site models, transport models, and other such sources generally are used to identify matrices of concern. It is critical to be as specific as possible when identifying a matrix.

From an analytical perspective, information on the chemical and physical characteristics of a matrix is extremely useful. Therefore, in addition to identifying the matrices of concern, every effort should be made to obtain any information available on the chemical and physical characteristics of the matrices. This information is particularly important when determining the required specificity of the analytical protocol, i.e., the ability to accommodate possible interferences. It is also important to identify any possible hazards associated with the matrix, such as the presence of explosive or other highly reactive chemicals. Issues related to specific matrices, such as filtration of water samples and removal of foreign material, are discussed in more detail in Section 3.5 and in Section 6.5.1.1 of Chapter 6.

OUTPUT: A list of the matrices of concern along with any information on the chemical and physical characteristics of the matrices and any information on possible hazards associated with them. As previously noted, the list of matrices of concern and the analyte list often are developed concurrently. In some cases, one analyst list is applicable to all the matrices of concern, and in other cases there are variations in the analyte lists for each matrix.

3.3.4 Determine Relationships Between the Radionuclides of Concern

Known or expected relationships among radionuclides can be used to establish "alternative" radionuclides that may be easier and less costly to measure. In most cases, an "easy-to-measure" radionuclide is analyzed, and the result of this analysis is used to estimate the concentration of one or more radionuclides that may be difficult to measure or costly to analyze.

One of the best known and easiest relationships to establish is between a parent radionuclide and its associated progeny. Once equilibrium conditions have been established, the concentration of any member of the decay series can be used to estimate the concentration of any other member of the series. For example, the thorium decay series contains 12 radionuclides. If each radionuclide in this series is analyzed separately, the analytical costs can be very high. However, if equilibrium conditions for the decay series have been established, a single analysis using gamma spectrometry may be adequate for quantifying all of the radionuclides in the series simultaneously.

Similarly, process knowledge can be used to predict relationships between radionuclides. For example, in a nuclear power reactor, steel may become irradiated, producing radioactive isotopes of the elements present in the steel. These isotopes often include ^{60}Co, ^{63}Ni, and ^{55}Fe. ^{60}Co decays by emission of a beta particle and two high-energy gamma rays, which are easily measured using gamma spectrometry. ^{63}Ni also decays by emission of a beta particle but has no associated gamma rays. ^{55}Fe decays by electron capture and has several associated X-rays with very low energies. Laboratory analysis of ^{63}Ni and ^{55}Fe typically is time-consuming and expensive. However, since all three radionuclides are produced by the same mechanism from the same source material, there is an expected relationship at a given time in their production cycle. Once the relationship between these radionuclides has been established, the ^{60}Co concentration can be used to estimate the concentration of ^{63}Ni and ^{55}Fe.

The uncertainty in the concentration ratio between radionuclide concentrations used in the alternate analyte approach should be included as part of the combined standard uncertainty of the analytical protocol in the measurement process. Propagation of uncertainties is discussed in Chapter 19.

OUTPUT: A list of known radionuclide relationships (e.g., those based on parent-progeny relationships or previous study results) and a list of potential radionuclide relationships (i.e., based on process knowledge). A preliminary study to determine the project-specific radionuclide relationships may be necessary, and additional measurements may be required to confirm the relationship used during the project. This information may be used to develop a revised analyte list.

3.3.5 Determine Available Project Resources and Deadlines

The available project resources can have a significant impact on the selection or development of analytical protocols, as well as the number and type of samples to be analyzed. In addition, project deadlines, and, in particular, required analytical turnaround times (see Section 6.5.3), can be important factors in the selection and development of analytical protocols for a particular project. During a directed planning process, radioanalytical specialists can provide valuable information on typical costs and turnaround times for various types of laboratory analyses.

OUTPUT: A statement of the required analytical turnaround times for the radionuclides of concern and the anticipated budget for the laboratory analysis of the samples.

3.3.6 Refine Analyte List and Matrix List

As additional information about a project is collected, radionuclides may be added to or removed from the analyte list. There may be one analyte list for all matrices or separate lists for each matrix. Developing an analyte list is an iterative process, however. The list should become more specific during the project planning process.

Radionuclides might be added to the analyte list when subsequent investigations indicate that additional radionuclides were involved in a specific project. In some cases, radionuclides may be removed from the analyte list. When the initial analyte list is compiled, there may be significant uncertainty associated with the presence of specific radionuclides. These radionuclides may be included on the analyte list to be conservative, even when there is only a small probability they may be present. Subsequent investigations may determine if specific radionuclides are actually present and need to be considered as part of the project. For example, a research laboratory was licensed for a specific level of activity from all radionuclides with atomic numbers between 2 and 87. Even limiting the analyte list to radionuclides with a half-life greater than six months provides several dozen radionuclides. A study may be designed to identify the actual radionuclides of concern through the use of historical records and limited analyses to justify removing radionuclides from the analyte list.

OUTPUT: A revised analyte list. Radionuclides can always be added to or removed from the analyte list, but justification for adding or removing radionuclides should be included in the project documentation.

3.3.7 Method Performance Characteristics and Measurement Quality Objectives

The output of a directed planning process includes DQOs for a project. DQOs apply to all data collection activities associated with a project, including sampling and analysis. In particular, DQOs for data collection activities describe the overall level of uncertainty that a decisionmaker is willing to accept for project results. This overall level of uncertainty is made up of uncertainties from sampling and analysis activities.

Since DQOs apply to both sampling and analysis activities, what are needed from an analytical perspective are performance objectives specifically for the analytical process of a particular project. MARLAP refers to these performance objectives as measurement quality objectives. The MQOs can be viewed as the analytical portion of the overall project DQOs. In a performance-based approach, the MQOs are used initially for the selection and evaluation of analytical protocols and are subsequently used for the ongoing and final evaluation of the analytical data.

In MARLAP, the development of MQOs for a project depends on the selection of an action level and gray region for each analyte during the directed planning process. The term "action level" is used to denote the numerical value that will cause the decisionmaker to choose one of the alternative actions. The "gray region" is a set of concentrations close to the action level, where the project planning team is willing to tolerate a high decision error rate (see Chapter 2 and Appendices B and C for a more detailed discussion of action levels and gray region). MARLAP recommends that an action level and gray region be established for each analyte during the directed planning process.

MARLAP provides guidance on developing MQOs for select method performance characteristics such as:

- The method uncertainty at a specified concentration (expressed as an estimated standard deviation);

- The method's detection capability (expressed as the minimum detectable concentration, or MDC);

- The method's quantification capability (expressed as the minimum quantifiable concentration, or MQC);

- The method's range, which defines the method's ability to measure the analyte of concern over some specified range of concentration;

- The method's specificity, which refers to the ability of the method to measure the analyte of concern in the presence of interferences; and

- The method's ruggedness, which refers to the relative stability of method performance for small variations in method parameter values.

An MQO is a statement of a performance objective or requirement for a particular method performance characteristic. An example MQO for the method uncertainty at a specified concentration, such as the action level, would be: "A method uncertainty of 0.01 Bq/g or less is required at the action level of 0.1 Bq/g." A qualitative example of an MQO for method specificity would be "The method must be able to quantify the amount of ^{226}Ra present, given elevated levels of ^{235}U in the samples." MQOs may be quantitative or qualitative in nature.

The list provided in this section is not intended to be an exhaustive list of method performance characteristics, and for a particular project, other method performance characteristics may be important and should be addressed during the project planning process. In addition, one or more of the method performance characteristics listed may not be important for a particular project. From an analytical perspective, a key activity during project planning is the identification of important method performance characteristics and the development of MQOs for the method performance characteristics.

In addition to developing MQOs for method performance characteristics, MQOs may be established for other parameters, such as data quality indicators (DQIs). DQIs are qualitative and quantitative descriptors used in interpreting the degree of acceptability or utility of data. The principal DQIs are precision, bias, representativeness, comparability, and completeness. These five DQIs are also referred to by the acronym PARCC; the "A" stands for accuracy instead of bias, although both indicators are included in discussions of the PARCC parameters (EPA, 1998). Since the distinction between imprecision and bias depends on context, and since a reliable estimate of bias requires a data set that includes many measurements, MARLAP focuses on developing an MQO for method uncertainty. Method uncertainty effectively combines imprecision and bias into a single parameter whose interpretation does not depend on context. This approach assumes that all potential sources of bias present in the analytical process have

been considered in the estimation of the measurement uncertainty and, if not, that any appreciable bias would only be detected after a number of measurements of QC and performance evaluation samples have been performed. MARLAP provides guidance on the detection of bias, for example, during analytical protocol validation and evaluation (Chapters 6 and 7). However, the most likely time to detect, and possibly correct, an unanticipated bias is during data quality assessment (see Chapter 9).

While MARLAP does not provide specific guidance on developing MQOs for the DQIs, establishing MQOs for the DQIs may be important for some projects. *EPA Guidance for Quality Assurance Project Plans* (EPA, 1998) contains more information on DQIs. MARLAP provides guidance on developing MQOs for method performance characteristics in the next section.

3.3.7.1 Develop MQOs for Select Method Performance Characteristics

Once the important method performance characteristics for an analytical process have been identified, the next step is to develop MQOs for them. This section provides guidance on developing MQOs for the method performance characteristics listed in the previous section. As noted, other method performance characteristics may be important for a particular analytical process, and MQOs should be developed for them during project planning.

METHOD UNCERTAINTY

While measurement uncertainty is a parameter associated with an individual result and is calculated after a measurement is performed, MARLAP uses the term "method uncertainty" to refer to the predicted uncertainty of a measured value that would likely result from the analysis of a sample at a specified analyte concentration. Method uncertainty is a method performance characteristic much like the detection capability of a method. Reasonable values for both characteristics can be predicted for a particular method based on typical values for certain parameters and on information and assumptions about the samples to be analyzed. These predicted values can be used in the method selection process to identify the most appropriate method based on a project's data requirements. *Because of its importance in the selection and evaluation of analytical protocols and its importance in the evaluation of analytical data, MARLAP recommends that the method uncertainty at a specified concentration (typically the action level) always be identified as an important method performance characteristic, and that an MQO be established for it for each analyte.*

The MQO for the method uncertainty at a specified concentration plays a key role in MARLAP's performance-based approach. It effectively links the three phases of the data life cycle: planning,

implementation, and assessment. This MQO, developed during the planning phase, is used initially in the selection and validation of an analytical method for a project (Chapter 6). This MQO provides criteria for the evaluation of QC samples during the implementation phase (Appendix C and Chapter 7). It also provides criteria for verification and validation during the assessment phase (Chapter 8). The use of the project-specific MQOs for the method uncertainty of each analyte in the three phases of the life of a project, as opposed to arbitrary non-project-specific criteria, helps to ensure the generation of radioanalytical data of known quality appropriate for its intended use.

The MQO for method uncertainty for an analyte at a specified concentration, normally the action level, is related to the width of the gray region. The gray region has an upper bound and a lower bound. The upper bound typically is the action level. The width of the gray region is represented by the symbol Δ. See Appendix B for information on setting up a gray region.

Appendix C provides the rationale and detailed guidance on the development of MQOs for method uncertainty. Outlined below is MARLAP's recommended guideline for developing MQOs for method uncertainty when a decision is to be made about the mean of a population represented by multiple samples. Appendix C provides additional guidelines for developing MQOs for method uncertainty when decisions are to be made about individual items or samples.

If decisions are to be made about the mean of a sampled population, MARLAP recommends that the method uncertainty (u_{MR}) be less than or equal to the width of the gray region divided by 10 for sample concentrations at the upper bound of the gray region (typically the action level). If this requirement cannot be met, the project planners should require at least that the method uncertainty be less than or equal to the width of the gray region divided by 3 (Appendix C).

EXAMPLE

Suppose the action level is 0.1 Bq/g and the lower bound of the gray region is 0.02 Bq/g. If decisions are to be made about survey units based on samples, then the required method uncertainty (u_{MR}) at 0.1 Bq/g is

$$\frac{\Delta}{10} = \frac{0.1 - 0.02}{10} = 0.008 \text{ Bq/g}$$

If this uncertainty cannot be achieved, then a method uncertainty (u_{MR}) as large as $\Delta / 3 =$ 0.027 Bq/g may be allowed if more samples are taken.

In the example above, the required method uncertainty (u_{MR}) is 0.008 Bq/g. In terms of method selection, this particular MQO calls for a method that can ordinarily produce measured results with expected combined standard uncertainties (1σ) of 0.008 Bq/g or less at sample concentrations at the action level (0.1 Bq/g in this example). Although individual measurement uncertainties will vary from one measured result to another, the required method uncertainty is effectively a target value for the individual measurement uncertainties.

OUTPUT: MQOs expressed as the required method uncertainty at a specified concentration for each analyte.

DETECTION AND QUANTIFICATION CAPABILITY

For a particular project, the detection capability or the quantification capability may be identified as an important method performance characteristic during project planning. If the issue is whether an analyte is present in an individual sample and it is therefore important that the method be able to reliably distinguish small amounts of the analyte from zero, then an MQO for the detection capability should be established during project planning. If the emphasis is on being able to make precise measurements of the analyte concentration for comparing the mean of a sampled population to the action level, then an MQO for the quantification capability should be established during project planning.

Detection Capability

When decisions are to be made about individual items or samples (e.g., drinking water samples), and the lower bound of the gray region is at or near zero for the analyte of concern, the detection capability of the method is an important method performance characteristic, and an MQO should be developed for it. MARLAP recommends that the MQO for the detection capability be expressed as a required MDC (Chapter 19).

Outlined below is MARLAP's recommended guideline for developing MQOs for detection capability. Appendix C provides the rationale along with detailed guidance on the development of MQOs for detection capability.

If the lower bound of the gray region is at or near zero and decisions are to be made about individual items or specimens, choose an analytical method whose minimum detectable concentration is no greater than the upper bound of the gray region.[1]

[1] The MDC is defined as the analyte concentration at which the probability of detection is $1 - \beta$.

Quantification Capability

When decisions are to be made about a sampled population and the lower bound of the gray region is at or near zero for the analyte of concern, the quantification capability of the method is an important method performance characteristic and an MQO should be developed for it. MARLAP recommends that the MQO for the quantification capability be expressed as a required MQC (see Chapter 19).

Outlined below is MARLAP's recommended guideline for developing MQOs for quantification capability. The MQC, as used in the guideline, is defined as the analyte concentration at which the relative standard uncertainty is 10 percent (see Chapter 19). Appendix C provides the rationale along with detailed guidance on the development of MQOs for quantification capability.

If the lower bound of the gray region is at or near zero and decisions are to be made about a sampled population, choose an analytical method whose minimum quantifiable concentration is no greater than the upper bound of the gray region which is typically the action level.

If an MQO for method uncertainty has been established, then establishing an MQO for the quantification capability in terms of a required MQC is somewhat redundant since an MQC is defined in terms of a specified relative standard uncertainty. However, this method performance characteristic is included in MARLAP for several reasons. First, it has been included to emphasize the importance of the quantification capability of a method for those instances where the issue is not whether an analyte is present or not—for example measuring ^{238}U in soil where the presence of the analyte is given—but rather how precisely the analyte can be measured. Second, this method performance characteristic has been included so as to promote the MQC as an important method parameter. And last, it has been included as an alternative to the overemphasis on establishing required detection limits in those instances where detection (reliably distinguishing an analyte concentration from zero) is not the key analytical question.

OUTPUT: If the lower bound of the gray region is at or near zero, and decisions are to be made about a sample population, MQOs expressed as MQCs should be developed for each analyte. If the lower bound of the gray region is zero and decisions are to be made about individual items or specimens, MQOs expressed as MDCs should be developed for each analyte.

RANGE

Depending on the expected concentration range for an analyte (Section 3.3.2), the method's range may be an important method performance characteristic. Most radioanalytical methods are

capable of performing over a fairly large range of activity concentrations. However, if the expected concentration range is large for an analyte, the method's range should be identified as an important method performance characteristic and an MQO should be developed for it. The radioanalytical specialist on the project planning team will determine when the expected concentration range of an analyte warrants the development of an MQO for the method's range. Since the expected concentration range for an analyte is based on past data which may or may not be accurate, the MQO for the method's range should require that the method perform over a larger concentration range than the expected range. This will help prevent the selection of methods which cannot accommodate the actual concentration range of the analyte.

OUTPUT: MQOs for the method's concentration range for each analyte.

SPECIFICITY

Depending on the chemical and physical characteristics of the matrices, as well as the concentrations of analytes and the concentrations of other chemical constituents, the method's specificity may be an important method performance characteristic for an analytical process. Method specificity refers to the ability of the method to measure the analyte of concern in the presence of interferences. In order to determine if method specificity is an important method performance characteristic, the radioanalytical specialist on the project planning team will need information on expected concentration ranges of the analytes of concern and other chemical constituents in the samples (Section 3.3.2), along with information on the chemical and physical characteristics of the matrices (Section 3.3.3). If it is determined that method specificity is an important method performance characteristic, then an MQO should be developed for it. The MQO can be qualitative or quantitative in nature.

OUTPUT: MQOs for the method specificity for those analytes likely affected by interferences.

RUGGEDNESS

For a project which involves analyzing samples which are complex in terms of their chemical and physical characteristics, the method's ruggedness may be an important method performance characteristic. Method ruggedness refers to the relative stability of the method's performance when small variations in method parameter values are made, such as a change in pH, a change in amount of reagents used, etc. In order to determine if method ruggedness is an important method performance characteristic, the radioanalytical specialist on the planning team needs detailed information on the chemical and physical characteristics of the samples. If it is determined that method ruggedness is an important method performance characteristic, then an MQO should be

developed for it. The MQO may require performance data which demonstrates the method's ruggedness for specified changes in select method parameters. The statistical manual of the *Association of Official Analytical Chemists* (AOAC) and the *Standard Guide for Conducting Ruggedness Tests* ASTM E1169 provides guidance on ruggedness testing.

OUTPUT: MQOs for method ruggedness for specified changes in select method parameters.

3.3.7.2 The Role of MQOs in the Protocol Selection and Evaluation Process

Once developed, the MQOs become an important part of the project's APSs and are subsequently incorporated into project plan documents (Chapter 4) and into the analytical Statement of Work (Chapter 5). In MARLAP, MQOs are used initially in the selection, validation, and evaluation of analytical protocols (Chapters 6 and 7). In a performance-based approach, analytical protocols are either accepted or rejected largely on their ability or inability to meet the project MQOs.

3.3.7.3 The Role of MQOs in the Project's Data Evaluation Process

Once the analytical protocols have been selected and implemented, the MQOs and—in particular—the MQOs for method uncertainty, are used in the evaluation of the resulting laboratory data relative to the project's analytical requirements. The most important MQO for data evaluation is the one for method uncertainty at a specified concentration. It is expressed as the required method uncertainty (u_{MR}) at some concentration, normally the action level (for this discussion, it is assumed that the action level is the upper bound of the gray region). When the analyte concentration of a laboratory sample is less than the action level, the combined standard uncertainty of the measured result should not exceed the required method uncertainty.

For example, if the required method uncertainty is 0.01 Bq/g or less at an action level of 0.1 Bq/g, then for any measured result less than 0.1 Bq/g, the laboratory's reported combined standard uncertainty should be less than or equal to 0.01 Bq/g. When the concentration is greater than the action level, the combined standard uncertainty of the measured result should not exceed the relative value of the required method uncertainty. If the required method standard uncertainty is 0.01 Bq/g or less at an action level of 0.1 Bq/g (10 percent of the action level), then for any measured result greater than 0.1 Bq/g, the laboratory's reported combined standard uncertainty should be no greater than 10 percent of the measured result. If an expanded uncertainty is reported with each measured value, and the coverage factor is also specified, the combined standard uncertainty may be calculated and checked against the required value. The check described relies on the laboratory's estimate of its measurement uncertainty. Additional checks are needed to ensure that the uncertainties are not seriously underestimated.

Appendix C provides guidance on developing criteria for QC samples based on the MQO for method uncertainty. Specifically, Appendix C contains equations for determining warning and control limits for QC sample results based on the project's MQO for method uncertainty.

The following example illustrates the use of the MQO for method uncertainty in evaluating QC sample results. Chapter 8, *Data Verification and Validation,* provides guidance on developing validation criteria based on the MQO for the required method uncertainty.

EXAMPLE

Suppose the upper bound of the gray region (the action level) is 0.1 Bq/g, and the required method uncertainty (u_{MR}) at this concentration is 0.01 Bq/g, or 10 percent. A routine laboratory control sample (LCS) is prepared with an analyte concentration of 0.150 Bq/g. (For the purpose of this example the uncertainty in the spike concentration is assumed to be negligible.) The lab analyzes the LCS with a batch of samples and obtains the measured result 0.140 ± 0.008 Bq/g, where 0.008 Bq/g is the combined standard uncertainty (1σ).

Question: Is this LCS result acceptable?

Answer: The LCS result may be acceptable if it differs from the accepted true value by no more than three times the required method uncertainty at that concentration. In this example the required method uncertainty is 10 percent at 1.50 Bq/g. So, the LCS result is required to be within 30 percent of 1.50 Bq/g, or in the range 0.105–0.195 Bq/g. Since 0.140 Bq/g is clearly in the acceptance range, the data user considers the result acceptable. Note also that the laboratory's reported combined standard uncertainty is less than the required method uncertainty, as expected.

3.3.8 Determine Any Limitations on Analysis Options

With the outputs of the resolution of a number of key analytical planning issues, such as a refined analyte list, MQOs for the analyte list, known relationships between radionuclides of concern, a list of possible alternate analytes, required analytical turnaround times, the analytical budget, etc., the project planning team may choose to determine the analyses to be performed for the project and thereby limit the analysis options available to the laboratory. It should be emphasized that determining which analyses need to be performed is not the same as indicating that a particular analytical protocol or analytical method has to be used. With the exception of gross alpha and beta measurements and gamma spectrometry, *MARLAP uses the term "analysis" to refer to a*

radionuclide/matrix combination. Examples of analyses to be performed include ^{3}H in water, ^{90}Sr in milk, ^{238}Pu in soil, etc. Although determining the analyses to be performed during the planning process may seem inconsistent with a performance-based approach, the project planning team may determine the analyses to be performed or may decide to eliminate some analyses from consideration. This decision may be based on information obtained during project planning, such as the absence of equilibrium between the analyte and other radionuclides in its decay chain or the presence of other radionuclides known to cause spectral interferences. However, in the absence of such considerations, the project planning team should allow the laboratory the flexibility of selecting the analyses which meet the analytical requirements as contained in the Analytical Protocol Specifications.

The role of the radioanalytical specialist is critical in determining if any limitations on analytical options are necessary because of the many laboratory-related issues and factors involved. For example, if several of the radionuclides of concern on the target analyte list are gamma-emitters, the radioanalytical specialist can determine if gamma spectrometry is an appropriate analysis given the required MQOs, matrices of concern, possible spectral interferences, etc. The radioanalytical specialist may determine that not only is gamma spectrometry an appropriate analysis for the gamma-emitting radionuclides of concern, but since there is evidence that equilibrium conditions are present, the results for gamma spectrometry can be used for other radionuclides of concern in the same decay chain as the gamma-emitting radionuclides. In other instances, such as the use of gamma spectrometry to quantify ^{226}Ra in the presence of elevated levels of ^{235}U, the radioanalytical specialist may determine that gamma spectrometry is not an appropriate analysis due to possible spectral interferences. The following sections provide a brief overview of some analysis procedures.

3.3.8.1 Gamma Spectrometry

In general, gamma spectrometry has many advantages over other choices. It is capable of identifying and quantifying a large number of radionuclides. In comparison with other analyses, it offers a fairly quick turnaround time and, since limited sample manipulation is involved, it is relatively inexpensive, particularly compared to analyses which require sample dissolution and chemical separations. It also allows for the use of relatively large sample sizes, thereby reducing the measurement uncertainty associated with subsampling at the laboratory. However, given its many advantages, gamma spectrometry cannot be used to analyze for all radionuclides. For example, gamma spectrometry may not be able to achieve the project's MQOs, since some or all of the radionuclides of concern may not be gamma-emitters, interfering radionuclides may present problems, etc. The radioanalytical specialist on the planning team can evaluate the

appropriateness of the use of gamma spectrometry for some or all of the radionuclides on the analyte list or for alternate analytes.

3.3.8.2 Gross Alpha and Beta Analysis

Gross alpha and beta analysis provides information on the overall level of alpha- and beta-emitting radionuclides present in a sample. The analysis has the advantage of a relatively quick turnaround time and generally is inexpensive compared to other analyses. The analysis also has significant limitations. It does not identify specific alpha- and beta-emitting radionuclides, so the source of the overall alpha and beta radiation is not determined by the analysis. It does not detect contribution from low-energy beta-emitting radionuclides such as ^{3}H. The measurement uncertainty of the analysis, particularly for matrices other than water, tends to be larger than the measurement uncertainty of other analyses. However, even with these limitations, gross alpha and beta analysis can be an important and appropriate analysis for a project.

3.3.8.3 Radiochemical Nuclide-Specific Analysis

In many instances, due to the project's MQOs, the lack of an appropriate alternate analyte, the lack of equilibrium conditions, etc., radiochemical nuclide-specific analyses are required. This is often true when radionuclides such as ^{3}H, ^{14}C, ^{90}Sr, isotopes of Pu, ^{99}Tc, etc., are on the analyte list. These analyses generally involve more manipulation of the samples than do gamma spectrometry and gross alpha and beta analysis. These analyses often require sample dissolution and chemical separation of the radionuclides of concern. For liquid scintillation counting, distillation is usually required for water samples, and some oxidative/combustion procedure is usually required for solid samples. Because of this, these analyses generally have longer turnaround times and are more expensive than other analyses.

Given the many analytical factors and considerations involved, *the role of the radioanalytical specialist is critical to determining if any limitations on analysis options are necessary.*

OUTPUT: Any limitations on analysis options, if appropriate.

3.3.9 Determine Method Availability

After the required analyses have been determined along with the sample matrices, the required MQOs, the analytical turnaround times, etc., the radioanalytical specialist should be able to determine if there are analytical methods currently available to meet the project's requirements. There are a number of sources of radioanalytical methods, including those published by the

American Society of Testing and Materials (ASTM), *Standard Methods for the Examination of Water and Waste Water* (APHA/AWWA, 1992), methods published in scientific journals, methods published in laboratory procedure manuals, and those published by Federal and State agencies.

If there are no known analytical methods that would meet the project's analytical requirements, the project planning team must evaluate options. They may decide to reevaluate the analytical data requirements, such as the MQOs, to see if they can be changed to allow the use of existing methods or increase the analytical budget and project timeline to allow for method development.

OUTPUT: A statement of method availability.

3.3.10 Determine the Type and Frequency of, and Evaluation Criteria for, Quality Control Samples

There are three main types of laboratory QC samples—blanks, replicates, and spikes. In addition, there are different types of blanks, replicates, and spikes. For example, spikes can be matrix spikes, laboratory control samples, external performance evaluation samples, etc. Chapter 18 contains a detailed discussion of the different types of QC samples and the information they provide. Since the results of the three main types of QC samples often are used to evaluate different aspects of the analytical process, most projects should employ all three types as part of the QC process.

The frequency of laboratory QC sampling for a project essentially represents a compromise between the need to evaluate and control the analytical process and the resources available. In addition, the nature of the project and the intended use of the data will play a role in determining the frequency of QC samples required. For example, the frequency of QC samples for a project involving newly developed methods for analytes in a complex matrix normally should be greater than the frequency of QC samples for a project using more established methods on a simpler matrix, assuming the intended use of the data is the same for both projects. The radioanalytical specialists on the project planning team play a key role in determining the type and frequency of QC samples for a project.

In order to adequately evaluate laboratory data, it is important that the QC samples be clearly linked to a group of project samples. Typically, this is done by analyzing QC samples along with a batch of samples and reporting the results together.

In addition to determining the type and frequency of QC samples, evaluation criteria for the QC sample results should be developed during the directed planning process and incorporated into the project's APSs. Appendix C provides guidance on developing criteria for QC samples and contains equations that calculate warning and control limits for QC sample results based on the project's MQO for method uncertainty.

OUTPUT: List of type and frequency of QC samples required and the criteria for evaluating QC sample results.

3.3.11 Determine Sample Tracking and Custody Requirements

A procedural method for sample tracking should be in place for all projects so that the proper location and identification of samples is maintained throughout the life of the project. Sample tracking should cover the entire process from sample collection to sample disposal. For some projects, a Chain-of-custody (COC) process is needed. COC procedures are particularly important in demonstrating sample control when litigation is involved. In many cases, Federal, State, or local agencies may require that COC be maintained for specific samples. Chapter 10, *Field and Sampling Issues that affect Laboratory Measurements*, provides guidance on sample tracking and COC. It is important that the requirements for sample tracking be clearly established during project planning.

OUTPUT: Project sample tracking requirements.

3.3.12 Determine Data Reporting Requirements

The data reporting requirements should be established during project planning. This involves determining not only what is to be reported but also how it is to be reported. Items that are routinely reported are listed below. It should be noted that this is not a comprehensive list, and some projects may require the reporting of more items while other projects may require the reporting of fewer items:

- Field sample identification number
- Laboratory sample identification number
- Sample receipt date
- Analysis date
- Radionuclide
- Radionuclide concentration units
- Sample size (volume, mass)

- Aliquant size (volume, mass)
- Radionuclide concentration at specified date
- Combined standard uncertainty or expanded uncertainty (coverage factor should be indicated)
- Sample-specific minimum detectable concentration
- Analysis batch identification
- Quality control sample results
- Laboratory instrument identification
- Specific analytical parameters (e.g., chemical yields, counting times, etc.)
- Analytical method/procedure reference

It is important that the required units for reporting specific items be determined during project planning. MARLAP recommends that units of the International System of Units (SI) be used whenever possible. However, since regulatory compliance levels are usually quoted in traditional radiation units, it may be appropriate to report in both SI and traditional units, with one being placed in parenthesis. *MARLAP also recommends that all measurement results be reported directly as obtained, including negative values, along with the measurement uncertainty—for example 2σ, 3σ, etc*. Additional guidance on data reporting, including a discussion of electronic data deliverables, is provided in Chapter 17, *Data Acquisition, Reduction, and Reporting,* and in Chapter 5, *Obtaining Laboratory Services*.

OUTPUT: Data reporting requirements for a project.

3.4 Matrix-Specific Analytical Planning Issues

This section discusses a number of matrix-specific analytical planning issues common to many types of projects. For each matrix there is a discussion of several potential key analytical planning issues specific to that matrix. It should be noted that what may be a key analytical planning issue for one project, may not be a key issue for another project. The list of potential matrix-specific key analytical planning issues discussed in this section is summarized in Table 3.1. Table 3.1 is not a comprehensive list, but rather is an overview of some common matrix-specific planning issues.

This section is divided into solids, liquids, filters and wipes. While filters and wipes are solids, they are discussed separately because of the unique concerns associated with them.

TABLE 3.1 — Matrix-specific analytical planning issues

MATRIX	RECOMMENDED KEY ISSUES	POTENTIAL KEY ISSUES
Solids (soil, sediment, structural material, biota, metal, etc.)	Homogenization Subsampling Removal of unwanted material	Container type Container material Sample preservation Screening samples for health and safety Volatile compounds Sample identification Cross-contamination Sample size Compliance with radioactive materials license Compliance with shipping regulations Chemical and physical form of the substrate
Liquids (drinking water, groundwater, precipitation, solvents, oils, etc.)	Is filtering required? Sample preservation Should sample be filtered or preserved first?	Sample identification Volume of sample Immiscible layers Precipitation Total dissolved solids Reagent background Compliance with radioactive materials license Compliance with shipping regulations
Filters and Wipes	Filter material Pore size Sample volume or area wiped	Sample identification Compliance with radioactive materials license Compliance with shipping regulations Subsampling Background from filter material

3.4.1 Solids

Solid samples consist of a wide variety of materials that include soil and sediment; plant and animal tissue; concrete; asphalt; trash, etc. In general, most solid samples do not require preservation (Chapter 10) but do require specific processing both in the field and in the laboratory. In certain instances, some biota samples may require preservation, primarily in the form of lowered temperatures, to prevent sample degradation and loss of water. Some common analytical planning issues for solid samples include homogenization and subsampling (Section 3.4.1.1) and the removal of unwanted materials (Section 3.4.1.2). For certain types of biological samples, removal and analysis of edible portions may be a key analytical planning issue.

Other issues that may represent key analytical issues for solids include container type and material (Chapter 10); sample preservation (Chapter 10); sample drying—wet, dry, ashed weights and ratios—(Chapter 10), screening samples for health and safety (Chapter 11); volatile compounds

(Chapter 10); sample identification (Chapters 10, 11, and 12); cross-contamination (Chapter 10); sample size (Chapters 10, 11, and 12); compliance with the radioactive materials license and shipping regulations (Chapter 11); and the chemical and physical form of the sample substrate (Chapters 13 and 14).

3.4.1.1 Homogenization and Subsampling

For many types of analyses, a portion of the sample sent to the laboratory must be removed for analysis. As with sampling in the field, this portion of the sample should be representative of the entire sample. Adequate homogenization and proper subsampling techniques are critical to obtaining a representative portion of the sample for analysis. Developing requirements for—and measuring the adequacy of—homogenization processes and subsampling techniques can be complicated for various types of solid matrices. General guidance on homogenization and subsampling is provided in Chapter 12 and Appendix F. The input of the radioanalytical specialist as a member of the project planning team is critical to developing requirements for homogenization processes and subsampling techniques.

3.4.1.2 Removal of Unwanted Materials

When a solid sample is collected in the field, extraneous material may be collected along with the "intended" sample. For example, when collecting a soil sample, rocks, plant matter, debris, etc., may also be collected. Unless instructed otherwise, samples received by the laboratory typically are analyzed exactly as they are received. Therefore, it is important to develop requirements regarding the treatment of extraneous materials. Ultimately, these guidelines should be based on the project's DQOs. The requirements should clearly state what, if anything, is to be removed from the sample and should indicate what is to be done with the removed materials. The guidelines should indicate where the removal process should occur (in the field, in the laboratory or at both locations) and the material to be removed should be clearly identified.

For soil samples, this may involve identifying rocks of a certain sieve size, plant matter, debris, etc., as extraneous material to be removed, weighed, and stored at the laboratory. For sediment samples, requirements for occluded water should be developed. In the case of biological samples, if the entire sample is not to be analyzed, the analytical portion should be identified clearly.

3.4.2 Liquids

Liquids include aqueous liquids (e.g., surface water, groundwater, drinking water, aqueous process wastes, and effluents), nonaqueous liquids (e.g., oil, solvents, organic liquid process wastes), and mixtures of aqueous and nonaqueous liquids.

A key analytical planning issue for most liquids is whether or not filtering is required or necessary; this is discussed in Chapter 10. The question of whether or not to filter a liquid is generally defined by the fundamental analytical question (Section 3.3.3). If the question is related to total exposure from ingestion, the liquids are generally not filtered or the filters are analyzed separately and the results summed. If the question is concerned with mobility of the analyte the concentration in the liquid fraction becomes more important than the concentration in the suspended solids (although some suspended solids may still be important to questions concerning mobility of contamination). In many projects, all of the liquids are filtered and the question becomes which filters need to be analyzed. Issues related to this decision include where and when to filter (Chapter 10); homogenization and subsampling (Chapter 10); volatile compounds (Chapter 10); screening for health and safety (Chapter 11); and cross-contamination (Chapter 10).

Another key analytical planning issue involves preservation of liquid samples, which is also discussed in Chapter 10. Sample preservation involves decisions about the method of preservation (temperature or chemical, Chapter 10), container type and material (Chapter 10), and chemical composition of the sample (Chapters 13 and 14). Preservation of radionuclides in liquids is generally accomplished in the same manner as preservation of metals for chemical analysis. There are of course exceptions such as for ^{3}H and ^{129}I.

A third key analytical issue results from the first two issues and involves the decision of which issue should be resolved first. Should the sample be filtered and then preserved, or preserved first and filtered later? This issue is also discussed in Chapter 10. In general, acid is used to preserve liquid samples. Since acid brings many radionuclides into solution from suspended or undissolved material, filtering is generally performed in the field prior to preserving the sample with acid.

Other analytical planning issues that may be important for a specific project include: sample identification (Chapters 10, 11, and 12); volume of sample (Chapter 10); compliance with radioactive materials license and shipping regulations (Chapter 11); immiscible layers (for mixtures of aqueous and nonaqueous liquids, Chapter 12); precipitation between filtration and analysis (Chapter 12); total dissolved solids (Chapter 12); and reagent background (Chapter 12).

3.4.3 Filters and Wipes

Filters include a wide variety of samples, including liquid filters, air filters for suspended particulates, and air filters for specific compounds. Once the decision to filter has been made, there are at least three key analytical planning issues: filter material, pore size, and volume of material to be filtered.

The selection of filter or wipe material can be very important. The wrong filter or wipe can dissolve, break, or tear, thus invalidating the sample. Chapter 10 includes a discussion of the various types of filter and wipe materials. Issues influencing this decision include the volume of material to be filtered, the loading expected on the filter, and the chemical composition of the material to be filtered.

The pore size is also important when preparing to filter. Too large a pore size will fail to collect all of the material that is needed, while too small a pore size may lead to clogged filters and reduced sample sizes. If an evaluation is being performed of respirable-size particles being released by a process, the pore size of the filter should reflect this requirement.

The volume of material to be filtered, or area to be wiped, is generally determined by the detection requirements for the project. Lower detection limits require larger samples. Larger samples may, in turn, result in problems with shipping samples or analytical problems where multiple filters were required to meet the requested detection limits.

Other analytical planning issues that may be important for a specific project include sample identification (Chapters 10, 11, and 12), compliance with radioactive materials license and shipping regulations (Chapter 11), and background contributions from filter materials (Chapter 12).

3.5 Assembling the Analytical Protocol Specifications

After key general and matrix-specific analytical planning issues have been identified and resolved, the next task of the project planning team is to organize and consolidate the results of this process into APSs for the project. In general, there will be an APS for each type of analysis (analyte-matrix combination). At a minimum, the APS should include the analyte list, the sample matrix, possible interferences, the MQOs, any limitations on analysis options, the type and frequency of QC samples along with acceptance criteria, and any analytical process requirements (e.g., sample tracking requirements). The analytical process requirements should be limited to only those requirements which are considered essential to meeting the project's analytical data requirements. For example, if the analyte of concern is known to exist in a refractory form in the

samples, then fusion for sample digestion may be included as an analytical process requirement. However, in a performance-based approach, it is important that the *level of specificity in the Analytical Protocol Specifications should be limited to those requirements which are considered essential to meeting the project's analytical data requirements*. The APS should be a one- or two-page form that summarizes the resolution of key analytical planning issues.

Figure 3.2 provides an example form for Analytical Protocol Specifications with references to sections in this chapter as major headers on the form. Figure 3.3 provides for the purpose of an example, an APS for ^{226}Ra in soil for an information gathering project.

3.6 Level of Protocol Performance Demonstration

As discussed in Section 3.3.7.3, during project planning, the project planning team should determine what level of analytical performance demonstration or method validation is appropriate for the project. The question to be answered is how the analytical protocols will be evaluated. There are three parts of this overall evaluation process: (1) the initial evaluation, (2) the ongoing evaluation, and (3) the final evaluation. This section briefly discusses the initial evaluation of protocol performance. Chapters 7 and 8 provide guidance on the ongoing and final evaluation of protocol performance, respectively.

The project planning team should determine what level of initial performance demonstration is required from the laboratory to demonstrate that the analytical protocols the laboratory proposes to use will meet the MQOs and other requirements in the APSs. The project planning team should decide the type and amount of performance data required. For example, for the analysis of ^{3}H in drinking water, the project planning team may decide that past performance data from the laboratory, such as the results of internal QC samples for the analysis of ^{3}H in drinking water, are sufficient for the initial demonstration of performance for the laboratory's analytical protocols if they demonstrate the protocol's ability to meet the MQOs. If the analysis is for ^{238}Pu in a sludge, the project planning team may decide that past performance data (if it exists) would not be sufficient for the initial demonstration of performance. The planning team may decide that satisfactory results on performance evaluation samples would be required for the initial demonstration of analytical protocol performance. Section 6.6 provides detailed guidance on protocol performance demonstration/method validation, including a tiered approach based on the project analytical needs and available resources.

Analytical Protocol Specifications

Analyte List: (Section 3.3.1, 3.3.7 **Analysis Limitations**: (Sections 3.3.9)

Matrix: (Section 3.3.3) **Possible Interferences**: (Sections 3.3.3, 3.3.5)

Concentration Range: (Section 3.3.2) **Action Level** (Section 3.3.8)

MQOs:

(Section 3.3.8) (Section 3.3.8)

(Section 3.3.8) (Section 3.3.8)

QC Samples		
Type	**Frequency**	**Evaluation Criteria**
(Section 3.3.11)	(Section 3.3.11)	(Section 3.3.8.2)
(Section 3.3.11)	(Section 3.3.11)	(Section 3.3.8.2)
(Section 3.3.11)	(Section 3.3.11)	(Section 3.3.8.2)
(Section 3.3.11)	(Section 3.3.11)	(Section 3.3.8.2)

Analytical Process Requirements*	
Activity	**Special Requirements**
Field Sample Preparation and Preservation	(Section 3.4)
Sample Receipt and Inspection	(Section 3.4.12)
Laboratory Sample Preparation	(Section 3.4)
Sample Dissolution	(Section 3.4)
Chemical Separations	(Section 3.4)
Preparing Sources for Counting	(Section 3.4)
Nuclear Counting	(Section 3.4)
Data Reduction and Reporting	(Section 3.3.13)
Sample Tracking Requirements	(Section 3.3.12)
Other	

*****Consistent with a performance-based approach, analytical process requirements should be kept to a minimum, therefore none or N/A may be appropriate for many of the activities.

FIGURE 3.2 — Analytical protocol specifications

Analytical Protocol Specifications (Example)

Analyte List: ^{226}Ra

Analysis Limitations: Must perform direct measurement of analyte or analysis of progeny allowed if equilibrium established at laboratory

Matrix: Soil

Possible Interferences: Elevated levels of ^{235}U

Concentration Range: 0.01 to 1.50 Bq/g

Action Level: 0.5 Bq/g

MQOs:

A method uncertainty (u_{MR}) of 0.04 Bq/g or less at 0.5 Bq/g

QC Samples		
Type	**Frequency**	**Evaluation Criteria**
Method blank	1 per batch	See attachment B*
Duplicate	1 per batch	See attachment B*
Matrix Spike	1 per batch	See attachment B*

Analytical Process Requirements	
Activity	**Special Requirements**
Field Sample Preparation and Preservation	None
Sample Receipt and Inspection	None
Laboratory Sample Preparation	None
Sample Dissolution	None
Chemical Separations	None
Preparing Sources for Counting	None
Nuclear Counting	None
Data Reduction and Reporting	See attachment A*
Sample Tracking Requirements	Chain-of-Custody
Other	

* Attachments A and B are not provided in this example

FIGURE 3.3 — Example analytical protocol specifications

3.7 Project Plan Documents

Once the APSs have been completed, they should be incorporated into the appropriate project plan documents and, ultimately, into the analytical Statement of Work. Chapters 4 and 5 provide guidance on the development of project plan documents and analytical Statements of Work, respectively. While the APSs are concise compilations of the analytical data requirements, the appropriate plan documents should detail the rationale behind the decisions made in the development of the APSs.

Summary of Recommendations

- MARLAP recommends that any assumptions made during the resolution of key analytical planning issues are documented, and that these assumptions are incorporated into the appropriate narrative sections of project plan documents.
- MARLAP recommends that an action level and gray region be established for each analyte during the directed planning process.
- MARLAP recommends that the method uncertainty at a specified concentration (typically the action level) always be identified as an important method performance characteristic, and that an MQO be established for it for each analyte.
- MARLAP recommends that the MQO for the detection capability be expressed as a required minimum detectable concentration.
- MARLAP recommends that the MQO for the quantification capability be expressed as a required minimum quantifiable concentration.
- MARLAP recommends that units of the International System of Units (SI) be used whenever possible.
- MARLAP recommends that all measurement results be reported directly as obtained, including negative values, along with the measurement uncertainty.

3.8 References

American Public Health Association, American Water Works Association, Water Environment Federation (APHA/AWWA). *Standard Methods for the Examination of Water and Wastewater*, 18th ed, 1992. American Public Health Association, Washington, DC.

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